

H-theorem and Thermodynamics for generalized entropies that depend only on the probability

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We consider a previously proposed non-extensive statistical mechanics in which the entropy depends only on the probability, this was obtained from a $f(\beta)$ distribution and its corresponding Boltzmann factor. We show that the first term correcting the usual entropy also arises from several $f(\beta)$ distributions, we also construct the corresponding H function and demonstrate that a generalized H -theorem is fulfilled. Furthermore, expressing this H function as function of the simplest Maxwellian state we find, up to a first approximation some modified thermodynamic quantities for an ideal gas. In order to gain some insight about the behavior of the proposed generalized statistics, we present some simulation results for the case of a square-well and Lennard-Jones potentials, showing that an effective repulsive interaction is obtained with the new formalism.

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I. INTRODUCTION

By considering non equilibrium systems with a long-term stationary state that possess a spatio-temporally fluctuating intensive quantity, more general statistics can be formulated, called Superstatistics [1]. Selecting the temperature as a fluctuating quantity among various available intensive quantities; in [2] a formalism was developed to deduce entropies associated to the Boltzmann factors $B(E)$ arising from their corresponding assumed $f_q(\beta)$ distributions. Following this procedure, the Boltzmann-Gibbs entropy and the Tsallis entropy S_q corresponding to the Gamma distribution (χ^2) and depending on a constant parameter q , were obtained. For the log-normal, F -distribution and other distributions it is not possible to get closed analytic expression for their associated entropies and the calculations were performed numerically utilizing the corresponding $B(E)$ in each case.

All these $f_q(\beta)$ distributions and their Boltzmann factors $B_q(E)$ obtained from them, depend on a constant parameter q , actually the F -distribution also depends on a second constant parameter. Consequently the associated entropies depend on q . An extensive discussion exists in the literature analyzing the possible viability of these kind of models to explain several physical phenomena [3, 4].

In previous works [5, 6] we proposed a generalized Gamma distribution depending on a parameter p_l and calculated its associated Boltzmann factor. We were able to find an entropy that depends only on this parameter p_l . By means of maximizing the entropy, p_l was identified with the probability distribution. Furthermore, by

considering the corresponding generalization of the von Neumann entropy in [7] it was shown that this same modified von Neumann entropy can be found by means of a generalized Replica trick [7, 8].

Since the fundamental results of Boltzmann [9] obtained in the frame of diluted gases, it is known that H -theorem is one of the cornerstones of Statistical Mechanics and Thermodynamics. Considering a system of N hard spheres all of the same size with no interaction among them he showed that for the function $H(t) = \langle \ln f \rangle$, with $\langle \rangle$ denoting the ensemble average, it satisfies, $dH/dt \leq 0$, which in the frame of a local or global equilibrium, encodes the first microscopic basis for the second law of thermodynamics. In general, the function H dictates the evolution of an arbitrary initial state for a gas into local equilibrium with the subsequent arrival to thermodynamic equilibrium. Several extensions to the H -theorem are known. A quantum version of the theorem was given by Pauli in the early 20's [10] and the first special relativistic version was presented by Marrot [11] with posterior modifications, within the special relativistic frame, introduced by several authors [12–14]. More recently, efforts to develop an H -theorem that takes into account other characteristics like frictional dissipation [15], leading to a modification of the classical non increase behavior for the H function, or a non-extensive quantum version [16] imposing a restrictive interval for the q parameter have been done.

In this work we follow the route of starting with a generalized H function which satisfies the H theorem, an entropy as a function of volume and temperature is obtained. Using this entropy, a broad thermodynamic information can be obtained. In the spirit of the original work of Boltzmann, an ideal gas is considered for the thermodynamical analysis. Some thermodynamic response functions are calculated presenting deviations with respect to conventional extensive quantities. Using the thermodynamic response functions and some approximations, we

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show that a modified non trivial equation of state can be obtained. More yet, a universal correction function emerge from this analysis for all the thermodynamical quantities.

We will first, in Section II, propose $f(\beta)$ distributions that do not depend on an arbitrary constant parameter, but instead on a parameter p_l that can be identified with the probability associated with the microscopic configuration of the system [6]. We will calculate the associated Boltzmann factors. It will be shown that for small variance of the fluctuations a universal behavior is exhibited by these different statistics. It should be noted that by changing in these $f(\beta)$ distribution p_l by $-p_l$ another family of Boltzmann factors with the same correction terms arise but now alternating the signs in the correction terms. We will not consider here these similar cases. In section III, a relevant result is obtained; in particular for the H associated with the Gamma (χ^2) distribution we will show a corresponding generalized H -theorem.

In section IV a calculation of the modified entropy, arising from the H -function, as a function of temperature and volume for an ideal gas is given. Thermodynamic response functions like heat capacity, and ratio of isothermal compressibility and thermal expansion coefficient are calculated and relative deviations of the usual behavior are discussed. Finally, some simulations results are given redefining the distribution probability using the generalized statistics. For the square-well and Lennard-Jones fluids, internal energies and heat capacities are given using both the standard Boltzmann-Gibbs statistics and generalized probability of this work. Section V is devoted to present our conclusions.

II. GENERALIZED DISTRIBUTIONS AND THEIR ASSOCIATED BOLTZMANN FACTORS

We begin by assuming a Gamma (or χ^2) distributed inverse temperature β depending on p_l , a parameter to be identified with the probability associated with the microscopic configuration of the system by means of maximizing the associated entropy. As the Boltzmann-factor is given by

$$B(E) = \int f(\beta) e^{-\beta E} d\beta. \quad (1)$$

We may write this parameter p_l Gamma distribution as

$$f_{p_l}(\beta) = \frac{1}{\beta_0 p_l \Gamma\left(\frac{1}{p_l}\right)} \left(\frac{\beta}{\beta_0} \frac{1}{p_l}\right)^{\frac{1-p_l}{p_l}} e^{-\beta/\beta_0 p_l}, \quad (2)$$

where β_0 is the average inverse temperature. Integration over β yields the generalized Boltzman factor

$$B_{p_l}(E) = (1 + p_l \beta_0 E)^{-\frac{1}{p_l}}, \quad (3)$$

as shown in [5], this kind of expression can be expanded for small $p_l \beta_0 E$, to get

$$B_{p_l}(E) = e^{-\beta_0 E} \left[1 + \frac{1}{2} p_l \beta_0^2 E^2 - \frac{1}{3} p_l^2 \beta_0^3 E^3 + \dots \right]. \quad (4)$$

We follow now the same procedure for the log-normal distribution, this can be written in terms of p_l as

$$f_{p_l}(\beta) = \frac{1}{\sqrt{2\pi} \beta [\ln(p_l + 1)]^{1/2}} \exp\left\{-\frac{\left[\ln \frac{\beta(p_l+1)^{1/2}}{\beta_0}\right]^2}{2 \ln(p_l + 1)}\right\}, \quad (5)$$

the generalized Boltzmann factor can be obtained to leading order, for small variance of the inverse temperature fluctuations,

$$B_{p_l}(E) = e^{-\beta_0 E} \left[1 + \frac{1}{2} p_l \beta_0^2 E^2 - \frac{1}{6} p_l^2 (p_l + 3) \beta_0^3 E^3 + \dots \right]. \quad (6)$$

In general, the F -distribution has two free constant parameters. We consider, particularly, the case in which one of these constant parameters is chosen as $v = 4$. For this value of the constant parameter we define a F -distribution in function of the inverse of the temperature and p_l as

$$f_{p_l}(\beta) = \frac{\Gamma\left(\frac{8p_l-1}{2p_l-1}\right)}{\Gamma\left(\frac{4p_l+1}{2p_l-1}\right)} \frac{1}{\beta_0^2} \left(\frac{2p_l-1}{p_l+1}\right)^2 \frac{\beta}{\left(1 + \frac{\beta}{\beta_0} \frac{2p_l-1}{p_l+1}\right)^{\left(\frac{8p_l-1}{2p_l-1}\right)}}, \quad (7)$$

once more the associated Boltzmann factor can not be evaluated in a closed form, but for small variance of the fluctuations we obtain the series expansion

$$B_{p_l}(E) = e^{-\beta_0 E} \left[1 + \frac{1}{2} p_l \beta_0^2 E^2 + \frac{1}{3} p_l \frac{(5p_l-1)}{p_l-2} \beta_0^3 E^3 + \dots \right]. \quad (8)$$

As shown in [5, 6] one can obtain in a closed form the entropy corresponding to (Eqs. 2, 3) resulting in

$$S = k \sum_{l=1}^{\Omega} (1 - p_l^{p_l}), \quad (9)$$

where k is the conventional constant and $\sum_{l=1}^{\Omega} p_l = 1$. The expansion of (Eq. 9) gives

$$-\frac{S}{k} = \sum_{l=1}^{\Omega} p_l \ln p_l + \frac{(p_l \ln p_l)^2}{2!} + \frac{(p_l \ln p_l)^3}{3!} + \dots \quad (10)$$

Given that the Boltzmann factors (Eqs. 4,6,8) coincide up to the second term for the Gamma (χ^2), log-normal and F -distributions, for enough small $p_l \beta_0 E$ the entropy (Eq. 10) correspond to all these distributions up to the first term that modifies the usual entropy. We expect at least this modification to the entropy for several possible $f(\beta)$ distributions.

III. A GENERALIZED H-THEOREM

The usual H-theorem is established for the H function defined as

$$H = \int d^3r d^3p f \ln f. \quad (11)$$

The essential of this theorem is to ensure that for any initial state, a gas that satisfies Boltzmann equation approach to a local equilibrium state, which means $dH/dt \leq 0$.

The new H function can be written as

$$H = \int d^3r d^3p (f^f - 1). \quad (12)$$

Considering the partial time derivative (because in general the gas is not homogeneous), we have

$$\frac{\partial H}{\partial t} = \int d^3r d^3p [\ln f + 1] e^{f \ln f} \frac{\partial f}{\partial t}. \quad (13)$$

Using the mean value theorem for integrals, and realizing that the factor $e^{f \ln f}$ is always positive, it follows from the conventional H-theorem that the variation of the new H-function with time satisfies

$$\frac{\partial H}{\partial t} \leq 0. \quad (14)$$

This is a very interesting result, we can see that other possible generalizations, for which the multiplying factor appearing in the integral is positive defined, will preserve the corresponding H-theorem.

IV. THERMODYNAMICS

It is well known that Boltzmann equation under very general considerations admits solutions with global existence and exponential or polynomial decays to Maxwellian states [17]. The simplest Maxwellian state among the five-parameter family is given by

$$f(\vec{p}) = n\Lambda^3 e^{-\frac{(\vec{p}-\vec{p}_0)^2}{2mkT}}, \quad (15)$$

where $n = N/V$, $\Lambda = \frac{h}{\sqrt{2\pi mkT}}$, with h the Planck's constant. Since this state is reached by the system under

very general conditions, we propose the new H function defined as

$$H = \int d^3r d^3p (e^{f \ln f} - 1), \quad (16)$$

by expanding and doing the corresponding integration, we obtain the exact relation

$$H = \sum_{l=1}^{\infty} \sum_{m=0}^l \frac{(-1)^m (2m+1)!}{(l-m)! m^{m+3/2} (m!)^2 2^{2m}} n^l \Lambda^{3(l-1)} (\ln n\Lambda^3)^{l-m}. \quad (17)$$

In order to get an insight into the new contributions coming from the generalized H-function to the thermodynamics of a system, we keep only the first terms of the previous series

$$H = n(\ln n\Lambda^3 - \frac{3}{2}) + \frac{n^2 \Lambda^3}{2^{5/2}} \left[(\ln n\Lambda^3)^2 - \frac{3}{2} \ln n\Lambda^3 + \frac{15}{16} \right]. \quad (18)$$

In the classical limit and for the system not far from equilibrium we have the proportionality between the H function and entropy

$$H = -\frac{S}{k}, \quad (19)$$

from which expression (18) multiplied by $-k$ gives the entropy (to the corresponding order) where the ideal contribution is given by $S_{ideal} = -kN(\ln n\Lambda^3 - \frac{3}{2})$ and the rest of the terms correspond to the corrections to the thermodynamics of the system. The extensivity property is broken by these new terms. We notice that the Sackur-Tetrode expression for the entropy of the ideal gas $S = kN \ln v + \frac{3kN}{2} \ln \frac{u}{b} + \frac{5kN}{2}$ can be recovered by an ad-hoc fixing term as it was originally proposed by Gibbs.

With the knowledge of the entropy as a function of volume and temperature it is possible to calculate some of the response functions for the system

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} C_V, \quad \left(\frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\kappa_T}, \quad (20)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad (21)$$

where α is the thermal expansion coefficient and κ_T is the isothermal compressibility. For an ideal gas $\alpha = 1/T$, $\kappa_T = 1/P$, therefore, using the equation of state $\alpha/\kappa_T = k_B n$, where k_B is the Boltzmann's constant and n is the number of moles. We obtain

$$\frac{C_V}{C_V^{ideal}} \sim 1 + \frac{n\Lambda^3}{2^{5/2}} \left[(\ln n\Lambda^3)^2 + \frac{1}{2} \ln n\Lambda^3 - \frac{9}{16} \right], \quad (22)$$

$$\frac{\left(\frac{\alpha}{\kappa_T}\right)}{\left(\frac{\alpha}{\kappa_T}\right)_{ideal}} \sim 1 + \frac{n\Lambda^3}{2^{5/2}} \left[(\ln n\Lambda^3)^2 + \frac{1}{2} \ln n\Lambda^3 - \frac{9}{16} \right], \quad (23)$$

The first contribution gives us the well known result for a classical ideal gas. It is remarkable that for both quantities the relative deviation from ideality have the same functional form. In fact, such deviation can be expressed in terms of only one variable (see Figure 1), $x \equiv n\Lambda^3$

$$F(x) \equiv \frac{x}{2^{5/2}} \left[(\ln x)^2 + \frac{1}{2} \ln x - \frac{9}{16} \right] \quad (24)$$

It can be observed that the usual behavior is obtained for very low densities or very high temperatures; deviations are expected for very low temperatures or very high densities. In particular, high densities could be achieved with very small volumes (for fixed N), i.e., for confined systems.

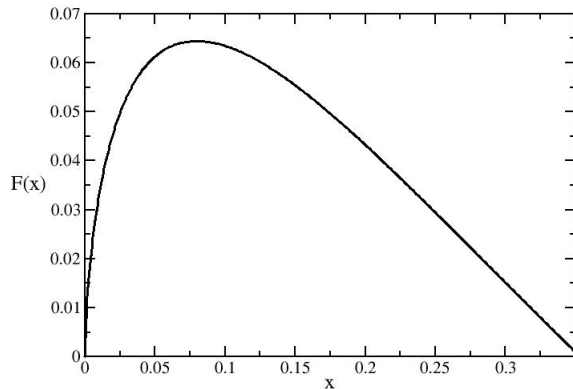


FIG. 1: Relative deviation from ideality for the thermodynamic quantities of the system. Ideal behavior is recovered for values of this function equal to zero.

It is a well known thermodynamic result that an equation of state (pressure as a function of volume and temperature) can be obtained if the response functions α and κ_T are given

$$dP = \frac{\alpha}{\kappa_T} dT - \frac{1}{V\kappa_T} dV, \quad (25)$$

in terms of the new variables (n, Λ) the change in pressure can be written as

$$dP = -\frac{h^2\Lambda^{-3}}{\pi m k} \frac{\alpha}{\kappa_T} d\Lambda + \frac{1}{n\kappa_T} dn, \quad (26)$$

and the response functions α, κ_T must be expressed in terms of n, Λ .

The quotient α/κ_T is known exactly, but the compressibility is not. It is possible to obtain an approximate equation of state considering an isochoric process, for it, an exact expression can be given (up to the considered order in our treatment). Even within this coarse approximation, a remarkable similar expression to the previous obtained for the heat capacity and the expansion coefficient is found. We can conjecture that the exact relative deviation for the pressure and the rest of the thermodynamic variables is given by the function $F(x)$ up to the considered order in the expansion resembling the universal behavior found for the distribution functions.

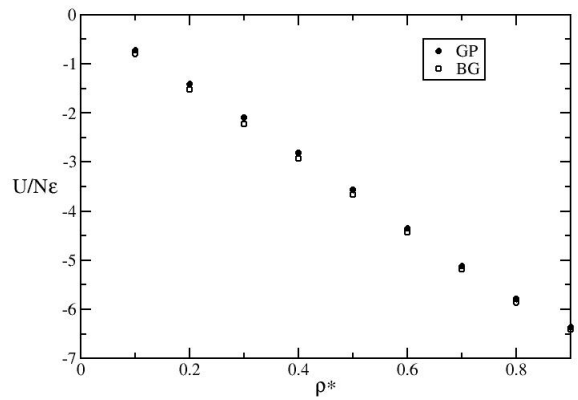


FIG. 2: NVT Monte Carlo simulation values for the Internal energy $U/N\epsilon$ for a system of $N = 500$ spherical particles of diameter σ interacting with a square-well potential with energy depth ϵ and attractive range $\lambda = 1.5\sigma$. Results are presented for a supercritical temperature $T^* = 2.0$, using the Boltzmann-Gibbs (BG) and generalized statistics (GP) with triangle and circle symbols, respectively. Auxiliary interpolating lines are used as a guide for a better visualization of the results.

In order to explore the consequences of redefining the distribution probability using a generalized statistics, we performed canonical ensemble Monte Carlo computer simulations for a fluid composed of spherical particles interacting via two different models, square-well (SW) and Lennard-Jones (LJ) potentials. In the first case we considered $N = 500$ particles of diameter σ interacting via a SW pair potential with an attractive range $\lambda = 1.5\sigma$ and energy-depth ϵ ; for the second model we used $N = 864$ particles. Results were obtained for the internal energy $U/N\epsilon$ and the constant-volume heat capacity $C_V^* = C_V/Nk$, using both the standard Boltzmann-Gibbs statistics and the generalized probability of this work [6], see Figures 2 and 3 for the SW system at temperature $T^* \equiv kT/\epsilon = 2.0$, and Figures 4 and 5 for the LJ system at temperatures $T^* = 1.2$ and $T^* = 1.5$. In the first case we are studying a supercritical temperature,

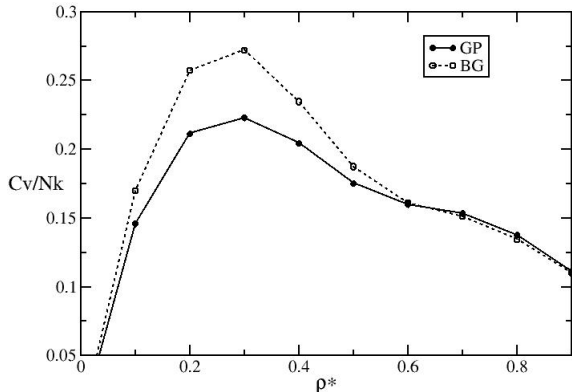


FIG. 3: NVT Monte Carlo simulation values for the constant-volume heat capacity C_V/Nk for a system of $N = 500$ spherical particles of diameter σ interacting with a square-well potential with energy depth ϵ and attractive range $\lambda = 1.5\sigma$. Results are presented for a supercritical temperature $T^* = 2.0$, using the Boltzmann-Gibbs (BG) and generalized statistics (GP) with black circle and open circle symbols, respectively. Auxiliary interpolating lines are used as a guide for a better visualization of the results.

whereas in the second case a comparison is made between a subcritical and supercritical case. In all the cases we observe that the generalized probability introduces an effective repulsive interaction. The effect on the thermodynamic properties is equivalent to increase the repulsive force between molecules and there is a reduction on the values for the internal energy. For the case of the heat capacity the effects of modifying the probability are more noticeable near the critical density or at higher densities where clearly the GP values of C_V^* are greater for the Boltzmann-Gibbs statistics. The procedure to define an effective potential $u_{eff}(r)$ is by assuming that the generalized Boltzmann factor in equation (4) can be mapped onto a classical Boltzmann factor,

$$e^{-\beta u_{eff}(r)} = B(E) \quad (27)$$

An interesting consequence of this effective-repulsive potential behavior is the possibility to map the thermodynamic properties of a GP system onto a BG one by modifying the potential parameters, like the diameter σ and range λ of the SW fluid. This type of mapping has been explored in the past in order to define the equivalence of thermodynamic properties between systems defined by different pair potentials [18], that now can be applied by mapping a GP and a BG potential-system.

If we think about the inverse problem, i.e., which is the pair potential that reproduces the experimental values of $U/N\epsilon$ or C_V/Nk of a real substance, it could be possible to assume that part of the information can be hindered in the statistical probability function used to obtain the information, i.e., to be considering either a BG statistics

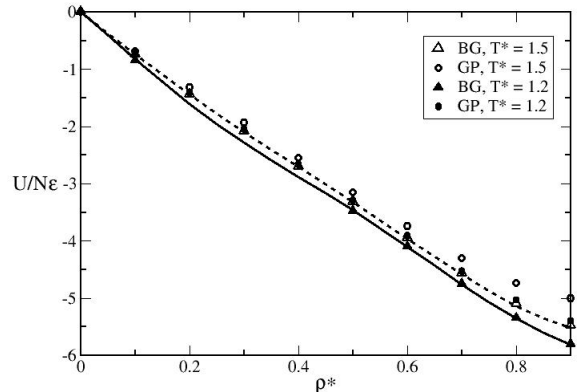


FIG. 4: NVT Monte Carlo simulation values for the internal energy $U/N\epsilon$ for a system of $N = 864$ particles interacting with a Lennard-Jones potential with energy depth ϵ and size parameter σ . Results are presented for a subcritical and a supercritical temperatures $T^* = 1.2$ and 1.5 , using the Boltzmann-Gibbs (BG) and generalized statistics (GP), as indicated in the figure. For the BG cases we include the corresponding predictions using the Lennard-Jones equation of state by Johnson *et al* in continuous and dashed lines for $T^* = 1.2$ and $T^* = 1.5$ respectively.[19]

with a specific potential model or a GP statistics with a modified pair potential.

V. CONCLUSIONS

Based on a non-extensive statistical mechanics generalization of the entropy that depends only on the probability, we show that the first term correcting the usual entropy also arises from several $f(\beta)$ distributions. We also construct the corresponding H -function and demonstrate that a generalized H -theorem is fulfilled. Furthermore, expressing this H function as a function of the simplest Maxwellian state we find, up to a first approximation some modified thermodynamic quantities for an ideal gas showing that a generic correction term appear, resembling the universal behavior founded for the distribution functions. Several simulation results are presented for internal energies and heat capacities for the square-well and Lennard-Jones potential. The simulation results support the theoretical results (for the ideal gas) showing that an effective repulsive interaction is obtained with the new formalism. Further research has to be done to elucidate the complete scenario proposed in this work.

Acknowledgments

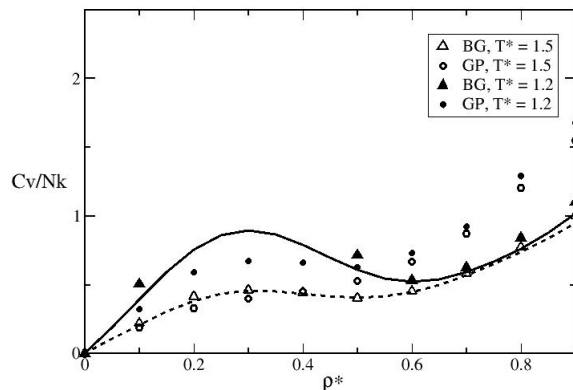


FIG. 5: NVT Monte Carlo simulation values for the constant-volume heat capacity C_V/Nk for a system of $N = 864$ particles interacting with a Lennard-Jones potential with energy depth ϵ and size parameter σ . Results are presented for a subcritical and a supercritical temperatures $T^* = 1.2$ and 1.5 , using the Boltzmann-Gibbs (BG) and generalized statistics (GP), as indicated in the figure. For the BG cases we include the corresponding predictions using the Lennard-Jones equation of state by Johnson *et al.* in continuous and dashed lines for $T^* = 1.2$ and $T^* = 1.5$ respectively.[19]

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